Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/materialsA

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Scalable one-step synthesis of TiO₂/WO₃ films on titanium plates with an efficient electron storage ability

Mingce Long,*^a Beihui Tan,^a Peidong Hu,^a Baoxue Zhou^a and Yongfeng Zhou^b

Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

We described a scalable method to synthesize TiO_2/WO_3 film electrodes through a one-step oxidation of Ti plates in a mixture of H_2O_2 and peroxotungstic acid solution. This composite film with a relatively low content of hexagonal 10 phase WO₃ displayed an excellent electron storage ability.

One interesting challenge in semiconductor photocatalysis is to extend their functions in the dark.¹ WO₃ shows an excellent electron storage ability by retaining negative charges in the framework of tungsten bronzes to neutralize the intercalated ¹⁵ cations, as shown in Eq. 1.^{1b} In absence of illumination, the stored electrons can be utilized in electron-mediated reactions, including the reduction of organic substrates or metal ions with proper reduction potentials,^{1c, 1d, 2} anticorrosion of stainless

- steel,^{1b} H₂ evolution,³ and bactericidal effect.^{1e} However, the poor ²⁰ photoactivity of WO₃ always results in a lower electron storage ability by itself. Using TiO₂ as the external electron source in photocharge stage becomes a promising strategy to enhance the energy storage performance. However, compared with the most commonly studied phases of amorphous and monolithic WO₃ in
- ²⁵ the TiO₂/WO₃ electrode,⁴ hexagonal form of WO₃ that displays excellent Li ion host ability has received little attention in the field of photogenerated electron storage.⁵

$$WO_3 + xe^- + xM^+ \frac{photocharge}{discharge} M_x WO_3$$
 (1)

Targeting on the electrical conversion and storage of solar 30 energy, it is crucial to synthesize photoanodes through a scalable method. Generally, the TiO2/WO3 photoanodes can be obtained by coating pre-synthesized nanocomposites or the physical mixture of TiO₂ and WO₃ on conductive glasses with separate steps. Using Ti plates as both the conducting substrate and the 35 titanium source is a promising strategy to synthesize TiO₂ photoelectrodes due to their excellent mechanical strength and conductivity.⁶ Unlike anodization involving electrochemical process, TiO₂ films generated by chemical oxidation of Ti plate in H₂O₂ shows such merits as no limitation of the reactor and the 40 applicable reaction conditions, which make this method potentially scalable. To further coupling TiO₂ with WO₃, post treatments including radio frequency (RF) sputtering technique, pulsed electrodeposition or wet impregnation are frequently applied.⁷ As we known, peroxotungstic acid (PTA) sol has been ⁴⁵ used as the precursor for WO₃ films or nanoparticles,⁸ and Ti

peroxy is also known as the intermediate of TiO₂ in the oxidation

of Ti plate in H₂O₂.⁹ Combining the two kinds of peroxy compounds, in this communication, we firstly reported a scalable one-step oxidation method without the involvement of any ⁵⁰ impurity compound to synthesize TiO₂/WO₃ film electrodes on Ti plates, and the presence of hexagonal WO₃ on the film at a relatively low content brought out an efficient electron storage ability.





In a typical synthesis, a peroxotungstic acid (PTA) sol (54 mM respect to W) was prepared firstly according to the modified previous method.^{8b} The cleansed Ti plate was soaked in H₂O₂ (5 st%) with the addition of various amount of PTA sol and maintained at 80 °C for 8 h in an airtight vial. Then the treated Ti plate was cleaned, dried and calcined at 400 °C for 2 h in an airtoven. The obtained samples were identified as TW1 and TW2 for the PTA concentration of 2.7 and 13.5 mM, respectively. For

75

comparisons, exclusively TiO_2 or WO_3 film (assigned as T or W) was prepared by following the same protocol in only H_2O_2 or PTA sol solution. According to the XRD patterns in **Fig. 1a**, besides the strong diffraction peaks of metallic Ti (JCPDS 44-

- s 1294), other peaks are unobservable for TiO₂, indicating that the amount of TiO₂ generated on the film is very low. This is consistent with the undergrown nanostructures of TiO₂ in the SEM images (**Fig. 1b**). The mild oxidation of Ti plate can be attributed to the relatively lower initial concentration of H_2O_2 .^{9a},
- ¹⁰ ¹⁰ With only PTA sol, a WO₃ film generates on Ti plate, whose XRD pattern can be attributed to the hexagonal WO₃ (JCPDS 33-1387), which is characterized by the hexagonal and trigonal tunnels originated from stacking WO₆ octahedra by sharing the axial oxygen along the c axis.⁵ Such tunnel structure was ¹⁵ expected having efficient electron storage ability because of its
- role as an excellent host to facilitate the diffusion of intercalation species.^{5b, 11} According to SEM (Fig. 1e) and TEM images (ESI, Fig. S1[†]), morphology of WO₃ on the film is characterized as the packing of micro-spherical aggregates of nanosheets with a width ²⁰ of about 100 nm and a length of about 800 nm.

The addition of PTA sol in H_2O_2 solution significantly promoted the oxidation of Ti plate. The characteristic peak at 25.1°, corresponding to the (101) plane of anatase TiO₂ (JCPDS 83-2243), emerges and increases in the patterns of TW1 and TW2,

- ²⁵ respectively. Moreover, a fully grown porous nanoflower structure with agglomerations of nanosheets can be observed in the SEM images of TW1 and TW2 (Fig. 1c and 1d). It should be noted that the introduction of PTA sol as the source of tungsten would decrease the initial pH of H_2O_2 solution (Table S1).
- ³⁰ According to the slightly increased diffraction intensity at 25.1° in XRD patterns of the films obtained by adjusting initial solution pH with HNO₃ or acetic acid (**ESI, Fig. S2**†), accelerated oxidation of Ti plates can be ascribed to both protons and PTA compounds. However, the intensity of the peak of anatase (101)
- ³⁵ plane in TW2 is about 2.8 times higher than the film obtained from the addition of HNO₃, indicating the PTA components play dominating role for the accelerated growth of TiO₂ on Ti plate. It was known that the initial oxidation of metallic Ti by H₂O₂ can be described by Eq. 2, while the decomposition of Ti peroxide by ⁴⁰ Eq. 3.⁹⁶

$$Surf(Ti) + H_2O_2 \to Surf(Ti)^+ + OH^- + OH \quad (2)$$
$$[Ti(IV)O_2]^{2+} + H^+ \to Ti(IV)^{4+} + HO_2^- \quad (3)$$

Increased protons in the solution would help the initial oxidation of metallic Ti (Eq. 2), inhibit the decomposition of the main ⁴⁵ oxidant HO₂⁻ (pKa=4.88), and facilitate the protonation of intermediates [Ti(IV)O₂]²⁺ and the generation of TiO₂•nH₂O (Eq. 3). Therefore, acidic conditions enhance the utilization efficiency of H₂O₂ and promote oxidation of Ti plate. On the other hand, It has been reported that the structure of PTA is like [(O₂)₂(O)W · ⁵⁰ O · W(O)(O₂)₂]^{2-.8a} Considering most oxidation intermediates of

- Titanium species in the Ti peroxy gel are positively charged, it can be expected that the neutralization of Ti and W peroxyl species would lead to polycondensation, coprecipitation and deposition of Ti and W oxides, as well as to promote the ⁵⁵ oxidation of metallic Ti. In addition, the observable peaks at 13.6° and 27.0° in the XBD pattern of TW2, corresponding to (100)
- and 27.9° in the XRD pattern of TW2, corresponding to (100) and (200) plane of hexagonal phase WO₃, respectively, indicate the existence of crystalized hexagonal WO₃ in the film TW2.

According to Scherrer's equation, the average primary particle $_{60}$ sizes were calculated as 14.1 nm and 12.6 nm for TiO₂ and WO₃ in TW2, respectively.

The film of TW2 was peeled off by sonication in alcohol, and one drop of the suspension was transferred to a grid for TEM observation. As shown in **Fig. 2a**, most of particles display ⁶⁵ nanosheet morphologies, with WO₃ nanoparticles dispersing over them. Two distinct regions with parallel fringes can be identified. The distances between the adjacent fringes of the two regions are determined to be about 0.352 and 0.634 nm (**Fig. 2b and c**), which can be ascribed to the interplaner distance of anatase TiO₂ 70 (101) and hexagonal WO₃ (100) planes, respectively. This indicates well contacts between TiO₂ and WO₃ nanostructures fabricated in TW2 film, and this is essentially important for charge transfer across the interface between different components.





Fig. 2. (a)TEM image of nanoparticles in TW2 film, (b, c) high resolution TEM images of part I and II in (a), (d) Raman so spectra of various films; (e) XPS spectrum of W 4d for TW2.

Raman spectra have been measured to provide further information on the surface compositions of films (**Fig. 2d**). Distinct characteristic bands at about 145, 398, 516, and 639 cm⁻¹ ⁸⁵ for the E_g, A_{1g}, B_{2g}, and E_g vibrational modes of anatase TiO₂, respectively, can be observed for both TW1 and TW2 films. Compared to those E_g mode of anatase TiO₂ in T film, the position for TW2 blue shifts from 147.5 to 143.6 cm⁻¹, and its full

width at half maximum (FWHM) broadens from 20.1 to 23.8 cm ¹. This could be the result of doped W atoms in the lattice of TiO₂.¹² Moreover, there are other obvious additional peaks of WO₃ in TW2 film. The band at 249 cm⁻¹ can be assigned to the 5 deformation vibration of O-W-O, while the other two bands at about 689 and 813 cm⁻¹ are attributed to the stretching vibration of bridging oxygen in W-O-W.^{7d, 8a, 11b} The absence of band at about 960 cm⁻¹ for stretching mode of W=O suggests the polymerization and deoxidization of PTA.^{8a, 11b} These bands are

- 10 characteristic features of hexagonal WO₃, which have already found broad applications in Li ion battery, gas sensor, electrochromic devices, and so on.^{5a, 11b} XPS spectrum of W 4d provided further evidence for the chemical state of W in TW2 film (Fig. 2e). The asymmetric peaks can be fitted into two pairs
- 15 of doublets. The more intense doublet at 247.8 and 260.2 eV can be attributed to W $4d_{5/2}$ and W $4d_{3/2}$ of W(VI) in WO₃, while the other doublet at 246.6 and 256.7 eV can be ascribed to those doped W(VI) atoms in TiO₂.¹³ The W(VI) atoms can easily enter the lattice of TiO₂ because of the similar sizes of W^{6+} (74.0 pm)
- ²⁰ and Ti⁴⁺ (74.5 pm), resulting in a higher electron density of W(VI) in the formation of W-O-Ti. Such bonded structure would also be expected to help charge transfer and increase tungsten utilization efficiency in photogenerated electrons storage. According to XPS analyses, the content of W in the film is estimated to be 7.78 wt%,
- $_{25}$ while the atomic percentage of W(VI) in WO₃ is as high as 85%, indicating WO₃ is dominated W(VI) in the film TW2.



³⁰ Fig. 3. (a) Changes in potential by photocharge for 400 s, and subsequently galvanostatic discharge at 10 µA•cm⁻² on various film electrodes in 0.1 M NaClO₄/ NaCOOH (pH=5.0). (b) Four cycles of on-off irradiation for TW2 film electrode by a two-electrode configuration. (+0.2 V bias vs. Pt counter electrode) 35

The films were directly used as working electrodes for

photocharge and galvanostatic discharge studies. Fig. 3a shows the potential shifts of T, TW1, TW2 and W films in the 40 photocharge and discharge processes. Upon illumination for 400 s, the potential negatively shift to -0.555, -0.639, -0.501 and -0.124 V vs. Ag/AgCl for T, TW1, TW2 and W electrodes, respectively. Moreover, W film with exclusively WO₃ displays obviously blue coloration after illuminated, representing the 45 formation of tungsten bronze (H_xWO₃). Theoretically, open circuit potential (Eoc) of illumined electrodes at sufficient high intensity should approach to the flatband potential (E_{FB}) of semiconductor oxide.¹⁴ TW2 electrode displays less cathodic potential than T and TW1, indicates electrons transfer from TiO₂ 50 to WO₃ and produce tungsten bronze when a significant amount of WO₃ presenting in the film. However, the formation of tungsten bronze would decrease the photooxidation activity of TiO₂ and reduce the photocurrent generation (ESI, Fig. S4 and S5†).4a,4b

When light is switch off, potential positively shifts more 55 than 0.3 V and 0.1 V in 60 s for T and TW1 films, respectively. The similar trend of rapid self-discharge suggests that potentials cannot be maintained for both T and TW1 films, which display negligible electron storage ability. However, only 0.015 V and 60 0.010V changes is observed for TW2 and W films, respectively. Moreover, both films displays a typical faradaic discharge behaviour in the galvanostatic discharge process, proofing the excellent ability to store electrons and retain potentials in dark. Although WO₃ has the photochromic effect for electron storage,

- 65 the low potential change upon irradiation indicates the photocharge ability of only WO₃ is poor, which can be attributed to the low photoactivity of WO₃ materials, as shown in the photocurrent transient (ESI, Fig. S4^{\dagger}). Coupling with TiO₂ to provide abundance photogenerated electrons is an effective way
- 70 to overcome such problem of WO₃. TW2 displayed an excellent charge-discharge performance, maintaining a high potential of -0.308 V after 5000 s discharge. It can be estimated that more than 0.05 C or $0.52 \text{ }\mu\text{mol}$ electrons per cm² have been stored in the film for discharged. The recyclability and stability of TW2 has 75 been further illustrated by a four-cycle test of on-off irradiation in a two-electrode configuration, as shown in Fig. 3b. The identical photocurrent generated at irradiation and the equivalent discharged electrons in dark indicate the good stability of TW2 electrode. Tungsten utilization efficiency (η_w) can be defined as
- 80 the ratio of the number of discharged electrons and the number of W atoms in the film, which is an indication of the electron storage capacity. Although it cannot be accurately obtained because of the uncertain amounts of oxides and tungsten atoms in the film, a high η_w can be expected due to the relatively low 85 content of tungsten, which are always higher than 20 wt% in previous reports that the electrode obtained from a mixture of TiO₂ and monolithic or amorphous WO₃.⁴ It is interesting there is few work discussing the hexagonal phase WO₃ in the electron storable TiO₂/WO₃ system. The high utilization efficiency of 90 tungsten in TW2 film can be attributed to the well contact
- interface between TiO₂ and WO₃ nanoparticles, the bonded format of W-O-Ti and the excellent proton host characteristic of hexagonal phase WO₃.

In summary, a one-step oxidation of Ti plate method was 95 successfully developed to synthesize TiO₂/WO₃ film, which can be directly used as photoanodes for solar energy conversion and storage. The presence of PTA sol promotes oxidation of Ti plate in H₂O₂ solution, and produces a composite film with an efficient and stable electron storage ability at a low amount of hexagonal

- 5 phase WO₃. This scalable method could be developed into an ondemand strategy by tuning the amount of tungsten source for photooxidation, photoelectrochemical or electron storage applications.
- Financial support from the Natural Science Foundation of 10 China (21377084), Shanghai Municipal Natural Science Foundation (13ZR1421000) and Special Fund for Agro-scientific Research in the Public Interest (201503107) is gratefully acknowledged.

15 Notes and references

- ^a School of Environmental Science and Engineering, Shanghai Jiao Tong University, Dongchuan Road 800, Shanghai 200240 (PR China). Fax: 86 21 54748025; Tel: 86 21 54747354; E-mail: long mc@sjtu.edu.cn ^b School of Chemistry and Chemical Technology, Shanghai Jiao Tong
- 20 University, Dongchuan Road 800, Shanghai 200240(PR China). † Electronic Supplementary Information (ESI) available: Experimental details, TEM of WO₃, XRD patterns of control samples, Raman spectrum, photocurrent transients, phenol photooxidations, elementary contents. See DOI: 10.1039/b00000x/
- 25
- (a) C. Ng, Y. H. Ng, A. Iwase and R. Amal, Phys. Chem. Chem. 1 Phys., 2011, 13, 13421; (b) T. Tatsuma, S. Saitoh, Y. Ohko and A. Fujishima, Chem. Mat., 2001, 13, 2838; (c) D. Su, J. Wang, Y. Tang, C. Liu, L. Liu and X. Han, Chem. Commun., 2011, 47, 4231;
- (d) I. Bedja, S. Hotchandani and P. V. Kamat, J. Phys. Chem., 30 199397, 11064; (e) T. Tatsuma, S. Takeda, S. Saitoh, Y. Ohko and A. Fujishima, Electrochem. Commun., 2003, 5, 793.
- 2 D. Zhao, C. C. Chen, C. L. Yu, W. H. Ma and J. C. Zhao, J. Phys. Chem. C. 2009. 113. 13160.
- 35 3 C. Ng, A. Iwase, Y. H. Ng and R. Amal, Chemsuschem, 2013, 6, 291.
- (a) S. Higashimoto, T. Shishido, Y. Ohno, M. Azuma, M. 4 Takahashi and M. Anpo, J. Electrochem. Soc., 2007, 154, F48; (b) S. Higashimoto, Y. Ushiroda and M. Azuma, Top. Catal., 2008, 47, 148; (c) H. Park, A. Bak, T. H. Jeon, S. Kim and W. Choi, 40
- Appl. Catal. B-Environ., 2012, 115, 74. 5 (a) S. Balaji, Y. Djaoued, A. Andre-Sebastien, R. Z. Ferguson and R. Brüning, Chem. Mat., 2009, 21, 1381; (b) M. Shibuya and M. Miyauchi, Chem. Phys. Lett., 2009, 473, 126.
- 45 6 (a) C. Mao, F. Zuo, Y. Hou, X. Bu and P. Feng, Angew. Chem., 2014, 53, 10485; (b) Y. H. Wu, M. C. Long, W. M. Cai, S. D. Dai, C. Chen, D. Y. Wu and J. Bai, Nanotechnology 2009, 20, 185703; (c) B. H. Tan, Y. Zhang and M. C. Long, Nanoscale Res. Lett. 2014, 9, 190; (d) X. J. Feng, J. M. Macak and P. Schmuki, Chem. Mat., 2007, 19, 1534. 50
- 7 (a) C. W. Lai, S. Sreekantan, E. Pei San and W. Krengvirat, Electrochim. Acta, 2012, 77, 128; (b) J. Wang, Y. Han, M. Feng, J. Chen, X. Li and S. Zhang, J. Mater. Sci., 2010, 46, 416; (c) S. Choudhary, S. Upadhyay, P. Kumar, N. Singh, V. R. Satsangi, R.
- Shrivastav and S. Dass, Int. J. Hydrog. Energy, 2012, 37, 18713; 55 (d) E. Valova, J. Georgieva, S. Armyanov, S. Sotiropoulos, A. Hubin, K. Baert and M. Raes, J. Electrochem. Soc., 2010, 157, D309
- 8 (a) K. Yamanaka, H. Oakamoto, H. Kidou and T. Kudo, Jpn. J. Appl. Phys., 1986, 25, 1420; (b) M. Yagi and S. Umemiya, J. Phys. 60 Chem. B, 2002, 106, 6355.
- 9 (a) J. M. Wu, T. W. Zhang, Y. W. Zeng, S. Hayakawa, K. Tsuru and A. Osaka, Langmuir, 2005, 21, 6995; (b) P. Tengvall, H. Elwing and I. Lundstrom, J. Colloid Interface Sci., 1989, 130, 405.
- 65 10 J. M. Wu, S. Hayakawa, K. Tsuru and A. Osaka, Cryst. Growth Des., 2002, 2, 147.

- 11 (a) L. Chen, S. Lam, Q. Zeng, R. Amal and A. Yu, J. Phys. Chem. C, 2012, 116, 11722; (b) A. Phuruangrat, D. J. Ham, S. J. Hong, S. Thongtem and J. S. Lee, J. Mater. Chem., 2010, 20, 1683.
- 70 12 (a) A. Fuerte, M. D. Hernandez-Alonso, A. J. Maira, A. Martinez-Arias, M. Fernandez-Garcia, J. C. Conesa, J. Soria and G. Munuera, J. Catal., 2002, 212, 1; (b) M. Fernandez-Garcia, A. Martínez-Arias, A. Fuerte and J. C. Conesa, J. Phys. Chem. B, 2005, 109, 6075
- 75 13 C. W. Lai and S. Sreekantan, Mater. Sci. Semicond. Process, 2013, 16.947.
- 14 (a) R. Beranek and H. Kisch, Electrochem. Commun., 2007, 9, 761; (b) Y. V. Pleskov, V. M. Mazin, Y. E. Evstefeeva, V. P. Varnin, I. G. Teremetskaya and V. A. Laptev, Electrochem. Solid-80 State Lett., 2000, 3, 141.